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Assessment of the Role of Nitrogen Oxides in Nonurban Ozone Formation

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16. ABSTRACT

This assessment is the fourth and final assessment of technical issues related to ozone and other photochemically generated products formed in the atmosphere requested by the Office of Air Quality Planning and Standards. A survey of information available on the role of NO_x in nonurban O_3 formation was prepared in 1979 (Martinez and Singh, 1979). This earlier survey was carried out to examine the hypothesis that NO_x was the limiting precursor species with respect to photochemical formation of O_3 over nonurban areas. If this hypothesis could be proved, it would indicate that increases in NO_x concentrations could lead to higher concentration levels of nonurban O_3. Because of the fragmentary knowledge of the interactions between NO_x and O_3 in nonurban areas, the authors of the survey could not arrive at any definite conclusions. However, this survey also included an interesting analysis of O_3 and NO_x measurements obtained from the Sulfate Regional Experiment (SURE) sites in the eastern United States. Additional experimental measurements, laboratory smog chamber results and modeling studies have become available during the last 5 years. These results have been discussed in a review (Altshuller 1984b) prepared on this subject. Based on these recent studies and earlier results a reevaluation of the factors influencing rural O_3 formation destruction and the role of NO_x in O_3 formation is provided in the present assessment.

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ENVIRONMENTAL RESEARCH BRIEF

Assessment of the Role of Nitrogen Oxides in Nonurban Ozone Formation

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Introduction

This is the fourth and final assessment of technical issues related to ozone and other photochemically generated products formed in the atmosphere. It was requested by the Office of Air Quality Planning and Standards. An earlier survey of information available on the role of NO_x in nonurban O_3 formation (Martinez and Singh, 1979) was conducted to examine the hypothesis that NO_x was the limiting precursor species with respect to photochemical formation of O_3 over nonurban areas. If proved, this hypothesis would indicate that increases in NO_x concentrations could lead to higher concentration levels of nonurban O_3, but because of fragmentary knowledge of the interactions between NO_x and O_3 in nonurban areas, the authors of the survey could not arrive at any definite conclusions.

Nevertheless, this survey also included an interesting analysis of O_3 and NO_x measurements obtained from the Sulfate Regional Experiment (SURE) sites in the eastern United States. Additional experimental measurements, laboratory smog chamber results, and modeling studies have become available during the last five years. These results have been discussed in a review (Altshuller 1984b) prepared on this subject. Based on these recent studies and earlier results, a reevaluation of the factors influencing rural O_3 formation destruction and the role of NO_x and O_3 formation is provided in the present assessment.

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Discussion of Issues

Three issues have been identified for consideration in this assessment. These issues concern both the characteristics of O_3 formation and transport over nonurban areas and the role of NO_x in processes leading to the O_3 formation that contributes to the observed O_3 concentrations.

Issue 1. Why are ozone concentrations exceeding 120 ppbv observed at some types of nonurban locations, but not at other nonurban locations in the United States?

Ozone concentrations exceeding 120 ppbv have been reported at nonurban locations in the northeastern, midwestern, and southeastern United States and in California. Some of these nonurban locations are within the interior of the continent, whereas others are at coastal sites. Ozone concentrations in excess of 120 ppbv have not been reported at nonurban locations scattered over large areas of the western United States. What conditions are consistent with these observations?

In a number of episodes, the elevated ozone concentrations observed were associated with the passage of urban plumes through the nonurban locations well downwind of the urban areas (Altshuller, 1984b). Elevated ozone concentrations have been observed during summer days after several hours of transport downwind in power plant plumes aloft within the eastern United States. However, evidence appears to be lacking on the ability of such plumes to fumigate ground level nonurban locations. Although some

elevation of ozone has been observed immediately downwind of large isolated industrial sources, there appears to be no evidence that such plumes can cause ozone concentrations in excess of 120 ppbv at nonurban locations well downwind.

There is evidence from both ground level measurements and aircraft measurements within urban plumes that ozone concentrations downwind on the same day as the plume left an urban area can exceed 120 ppbv at nonurban locations (Altshuller, 1984b). Smog chamber studies and photochemical model simulations also predict that such elevated ozone concentrations can occur downwind in urban plumes. The ground level observations of elevation of ozone in an urban plume fumigating a specific nonurban location in some episodes have been based on air quality measurements as well as back trajectory analyses.

Elevated ozone concentrations at nonurban locations associated with more than one day of transport over land are difficult to demonstrate except based on circumstantial evidence. It is very plausible that ozone demonstrated to be trapped aloft in the evening hours of one day and then subjected to high velocity nocturnal jet winds aloft should be transported overnight substantial distances downwind. The next morning breakup of the nocturnal surface inversion layer with strong vertical mixing during summer morning hours brings the ozone from aloft to the surface. There also are experimental results consistent with the survival of most of the ozone trapped aloft the previous night into the next morning. However, it has been impossible to associate clearly the elevated ozone at ground level the second day with a specific source area upwind.

Back trajectory analyses usually provide what evidence is available about the history of the air parcels reaching nonurban locations. However, the transport distances and directions predicted over multiday periods by back trajectory analyses are subject to substantial uncertainties. Within the eastern United States, many adjacent source areas and combinations of source areas exist. Small errors in back trajectory analyses could lead to misidentifications among such sources. Where flows coming from relatively unpolluted areas need to be distinguished from those coming from highly polluted areas and the quadrants from which the flows come are well separated, back trajectory analyses are less ambiguous. Back trajectories to unpolluted land areas upwind usually are not associated with elevated ozone concentrations.

Results from several smog chamber studies and modeling simulations of transport from urban areas are consistent with the observation of ozone concentrations above 120 ppbv downwind over land on the second day of transport. However, such modeling exercises usually have not attempted to simulate the details of dilution and deposition over multiday periods of transport over land areas.

Often elevated ozone concentrations within highly populated areas of the eastern United States are associated with the presence of a slowly moving high pressure system in the same region. Such summer high pressure systems are associated with periods of high temperature, nearly maximum available solar radiation, and low wind speeds. These conditions favor ozone formation within air parcels moving through the high pressure systems. At times the clockwise flow can cause the accumulated precursors and ozone from upwind to flow across a large urban area before reaching a nonurban location farther downwind. Such conditions are particularly favorable to high ozone concentrations being observed at such nonurban locations.

Aircraft traverses of urban plumes over nonurban areas in the eastern United States indicate that the ozone concentrations outside of the plumes are one-half to one-third the concentrations within the plumes (Altshuller, 1984b). Therefore, the ozone background concentration rarely exceeds 120 ppbv, although it can exceed 80 ppbv. Long-range aircraft traverses over the eastern United States on summer days during episodes of elevated ozone concentrations associated with high pressure systems indicate that these ozone concentrations ordinarily are below 120 ppbv. When the concentrations exceed 120 ppbv, they usually are associated with aircraft traverses across specific plumes from urban areas upwind. Such aircraft results are consistent with the relatively low frequency of ozone concentrations above 120 ppbv being observed at nonurban sites even within heavily populated regions of the eastern United States.

However, it should be noted that the frequency with which elevated ozone concentrations occur in the presence of high pressure systems can vary from one summer season to another. A critical factor appears to be the occurrence of macroscale high pressure systems having a period greater than 20 days.

Episodic periods occur during which elevated ozone concentrations, at times exceeding 120 ppbv, have been observed at sites with offshore winds on the east and west coasts of the United States. Aircraft flights over areas of the Atlantic Ocean and Gulf of Mexico on several occasions have resulted in observed ozone concentrations exceeding 120 ppbv (Altshuller, 1984b). Elevated ozone concentrations also have been observed at nonurban coastal locations in western Europe. On a few occasions the upwind transport has been tracked by aircraft. More usually the upwind transport is defined by back trajectory analyses. Such results indicate flow from heavily populated areas off-shore with transport over open water for 24 to 48 hours followed by on-shore flow in the vicinity of the monitoring location.

The persistence of ozone over water is consistent with the very low dry deposition rates for ozone over water. Ozone formation can continue at reduced rates with slow ozone depletion by chemical processes and with dilution by cleaner air from aloft. This combination of processes, when modeled for multiday periods over water, results in a slow depletion of ozone (Altshuller, 1984b). As a result, ozone concentrations after 24 to 48 hours of transport over water are only moderately lower than when the air parcels left land.

The ozone concentrations reported at monitoring locations in many remote areas of the western United States have not been reported as exceeding 120 ppbv and rarely exceed 80 ppbv (Altshuller, 1984b). Aircraft measurements of ozone

in the western United States usually result in the observation of low ozone concentrations. Therefore, evidence is lacking for fumigation of these western monitoring sites after multiday transport from distant urban areas. Such results are consistent with the following circumstances: (a) the small number of urban areas within 500 km of such monitoring sites, (b) the low population densities in the immediate areas of such sites, (c) the more rapid movement of high pressure systems in the western United States, reducing what accumulation of ozone and precurors may occur, (d) the substantial rate of dry deposition of ozone likely to occur during the summer months over such land areas, and (e) the spreading and dilution of isolated urban plumes under stable conditions experienced during multiday transport.

Issue 2. What processes for ozone formation contribute significantly to the longer time averaged ozone concentrations in nonurban areas?

Episodic peak-hour ozone concentrations and longer-time averaged O_3 levels are of some consequence to health and agriculture. Longer time exposures to ozone can result in yield reductions of field crops (Heck *et al.*, 1984; Skärby and Sellden, 1984) and may affect growth in forests (Skärby and Sellden, 1984). The most appropriate exposure statistics are still under evaluation (Skärby and Sellden, 1984; Larson and Heck, 1984). The mean O_3 concentrations associated with natural processes for O_3 formation can be of significance in the mathematical models used to estimate yield reductions for crops such as soybeans and cotton (Larson and Heck, 1984).

As discussed in the review paper (Altshuller, 1984b) and in issue 1 of this assessment, plumes from cities, towns, and industrial sources can frequently impact nonurban areas containing field crops or forests in the more heavily populated regions of eastern United States, and ozone formed within such plumes can contribute significantly to upper-percentile O_3 concentrations in these areas. However, even in the eastern United States the mean seasonal concentrations reported often are not much higher than in more lightly populated areas of the western United States.

An example is provided by the monitoring results of Decker and coworkers (1976). During the summer of 1975 the mean O_3 concentrations at two eastern locations, Bradford, PA, and Lewisburg, WV, were 41 and 38 ppbv, whereas at sites west of the Mississippi River, Creston, IA, and Wolf Point, MT, the mean O_3 concentrations were 35 and 29 ppbv. However, the O_3 concentrations above 70 ppbv were exceeded 7 to 8% of the time at Bradford, PA, and Lewisburg, WV; 2.3% of the time at Creston, IA; and 0.0% of the time at Wolf Point, MT. The much higher frequency of occurrence of somewhat elevated concentrations at the two eastern sites was influenced not only by higher population densities and more sources producing O_3-containing plumes but by the greater tendency for stagnation of high pressure systems in this region of the eastern United States (Korshover, 1975). Such slowly moving high pressure systems allow time for many sources to superimpose precursor emissions to O_3 formation in air parcels moving across the high pressure systems.

A very small spread in mean O_3 concentrations has been reported for a group of three nonurban monitoring locations in Minnesota and North Dakota (Pratt *et al.*, 1983). The sites ranged from 42 km out to 486 km from the Minneapolis-St. Paul metropolitan area. The mean O_3 concentrations over the 1977-1981 study period were 32.26 ppbv, 32.09 ppbv, and 32.42 ppbv. However, the site nearest the metropolitan area was more frequently fumigated by the urban plume, so that O_3 concentrations exceeding 70 ppbv were measured on a total of 368 hr. At the most remote site O_3 concentrations above 70 ppbv were measured for a total of 275 hr. This is not a large difference in frequency of occurrence. In such western areas only one or a few plumes are likely to fumigate a nonurban site, and stagnating high pressure systems are infrequent in western areas of the United States (Korshover, 1975).

Such results as those discussed above for mean O_3 concentrations can lead to the hypothesis that mean O_3 concentrations are predominately determined by natural sources of O_3 formation. This hypothesis would appear to have particular applicability in large, lightly populated agricultural areas west of the Mississippi River.

Two natural processes are frequently considered as to their significance in contributing to O_3 concentrations at ground level. One of these is transport of ozone from in lower stratosphere through the troposphere to ground level. In a recent assessment on this subject (Altshuller, 1984a) use of both the ^7Be to O_3 and ^{90}Sr to O_3 ratio techniques, as well as tropospheric modeling results lead to the estimate that 15 ppbv or less of the O_3 measured at ground level locations would be of stratospheric origin during the summer months. Since measured mean concentrations during the summer range from 29 to 45 ppbv, no more than one-third to one-half of the mean nonurban O_3 concentrations can be attributed to stratospheric O_3. The other natural process often considered is O_3 formation from biogenic hydrocarbons, isoprene and monoterpenes, reacting with NO_x. In general these reactions do not appear to account for a substantial part of the nonurban O_3 concentrations. Such a conclusion is based on estimates derived from the O_3-forming potential of the ambient air concentrations of biogenic hydrocarbons (Altshuller, 1983a) and on recent model results (Altshuller, 1984b). In particular it is the heavily forested areas, not the sparsely forested agricultural areas west of the Mississippi River, to which biogenic hydrocarbons are attributed. Finally, it should be noted that NO_x is crucial to O_3 formation from biogenic hydrocarbons, and the NO_x is predominately from anthropogenic sources throughout the United States (Altshuller, 1984a).

If the two natural processes discussed above are not likely to account for the major part of the mean O_3 concentrations measured, what process is responsible? The process most likely to account for a major part of the longer-time averaged O_3 concentrations in nonurban areas during the warmer months of the year is photochemical O_3 formation within the free troposphere (Altshuller, 1984a,b). Anthropogenically, emissions of carbon monoxide, non-methane hydrocarbons and NO_x constitute a major part of the precursors to O_3 formation in the free troposphere (Altshuller, 1984a). Predictions of O_3 concentrations by tropospheric models are strongly dependent on the vertical

NO_x concentration gradient assumed through the free troposphere. Comparisons of O_3 concentrations at mid-latitudes in the northern hemisphere compared to the southern hemisphere indicate that anthropogenic emissions may be associated with 20 to 25 ppbv of the O_3 formed in the free troposphere (Altshuller, 1984a). Since this estimate was based on modeling results obtained before anthropogenic non-methane hydrocarbons were included as precursors in a tropospheric model, the estimates may need to be increased moderately. Of course, in considering the contribution of free troposphere O_3 to ground level O_3, it is assumed that transport of O_3 between the free troposphere and the boundary layer readily occurs on a time averaged basis.

Substantial year to year variations in mean O_3 concentrations and in the frequency distribution of O_3 concentrations have been observed at a number of nonurban locations (Decker *et al.*, 1976; Pratt *et al.*, 1983; Mohnen, 1982). Such year to year variations can be greater than site to site variations within the same region during the same year (Pratt *et al.*, 1983). Variations in the frequency and duration of stagnating high pressure systems may explain such year to year variations in some of these locations (Decker *et al.*, 1976). However, such year to year variations also are observed in relatively remote areas not strongly influenced by stagnating high pressure systems (Pratt *et al.*, 1983). Therefore, year to year variations in the O_3 production in the free troposphere or in the O_3 transport from the lower stratosphere also may be in part responsible for such ground level O_3 concentration levels.

Issue 3. Is NO_x the precursor limiting ozone formation over nonurban areas of the United States?

Both hydrocarbons and nitrogen oxides serve as precursors to ozone production in nonurban areas. This is so both for ozone formation within the planetary boundary layer and in the free troposphere. Most hydrocarbons are consumed predominately by reactions with hydroxyl radicals. Olefinic hydrocarbons are consumed by reactions with both hydroxyl radicals and ozone. Nitrogen dioxide is converted reversibly to PANs by reactions with acyl peroxy radicals and irreversibly to nitric acid by reaction with hydroxyl radicals. Since the concentrations of all of the radical species vary with available solar light intensity, the lifetimes of hydrocarbons and nitrogen oxides should vary with season, latitude, and altitude. The reactivity of individual hydrocarbons with hydroxyl radicals or ozone varies greatly, resulting in lifetimes ranging from fractions of an hour for certain olefins to months for ethane and acetylene. The lifetime of NO_x has been estimated in smog chamber studies and from modeling simulations. Of particular interest are the estimates of NO_x lifetime obtained by measurements within urban plumes.

The lifetime of NO_2 under sunny summertime, moderately polluted conditions has been obtained by measurements within the plume of Boston as it was transported over the Atlantic Ocean (Altshuller, 1984b). Dilution was corrected for by use of one of several tracers which were inert over the experimental periods involved. These tracers were acetylene, carbon monoxide, and F-11. Based on these measurements the lifetimes (1/K) range from 4.2 to 7.1 hours and average 5.5 hours. Subsequent measurements over land in the Philadelphia plume calculated upper limits for NO_x lifetime of five and eight hours. Therefore, an average lifetime under the conditions of these experiments is near six hours. Since these measurements were made after the plume had left the city, the NO to NO_2 conversion time of one to three hours needs to be added to obtain NO_x lifetimes. The plume measurements over the ocean are particularly useful because dry deposition is minimized. The technique used cannot distinguish between losses of NO_x resulting and chemical reaction compared to deposition. In an urban plume simulation study, NO_x lifetimes consistent with these experimental results were obtained (Altshuller, 1984b).

Lifetimes of hydrocarbons, excepting ethene, were not estimated from the same field experiments. Hydrocarbon lifetimes can be estimated using ozone concentrations and estimates of hydroxyl radical concentrations (Altshuller, 1983c, 1984b). Alternatively, hydrocarbon lifetimes for the more reactive hydrocarbons can be obtained from smog chamber studies. Based on such estimates, the lifetimes of olefins other than ethene and of dialkyl and trialkylbenzenes are equal to or shorter than that of NO_x. From available estimates, the lifetime of ethene ranges from about that of NO_x to moderately longer than NO_x. The lifetimes of monoalkylbenzenes and of the most reactive alkanes during summer days are two to three times longer than that of NO_x. Hydrocarbons such as benzene, propane, butanes and pentanes have lifetimes of several days and longer.

There will be a continuing change in the composition of hydrocarbons and their ratios to NO_x as an urban plume travels downwind over water or lightly populated land areas. Over heavily populated land areas, these precursors may be somewhat depleted, but significant replenishment can occur from fresh emissions. Therefore, the life histories of plumes with respect to hydrocarbon concentrations and composition and ratios to NO_x within each plume should vary with plume transport time and direction. It should be noted that the most reactive hydrocarbon species are not necessarily the most abundant species, so their consumption may not reduce NMHC concentrations substantially. In addition, the oxygenated hydrocarbon products formed from the more reactive hydrocarbons will continue to contribute to the chemical reactivity of the plume for a number of additional hours. It is consistent with these changes in composition that as plumes age, NO_x eventually will become the limiting species with respect to ozone formation. Other information also must be considered to better determine when NO_x actually should become the limiting species with respect to ozone production.

The results of several smog chamber studies simulating first day irradiations indicate that ozone formation is not NO_x limited but, instead, ozone formation increases with decreases in NO_x concentration (Altshuller, 1983b, 1984b). The results obtained from chemical kinetic modeling and from statistical treatments of ambient air measurements are consistent with these smog chamber studies.

In a modeling simulation of urban plumes, NO_x also was not found to be limiting during the daylight hours of the first day. A fourfold increase in the HC/NO_x ratio substantially

increased the maximum ozone formed. Similarly a negative correlation was obtained between ozone and NO_x from local sources in statistical studies involved with analyzing the effects of precursor emissions into air parcels traveling with transport layer winds in the 300 m to 200 m altitudes.

For multiday transport the key factor is the short lifetime of NO_x. Both experimental plume studies and plume and air parcel model simulations indicate very little NO_x available by the evening of the first day. However, modeling studies indicate that PAN would serve as a reservoir for NO_x into the second day. Substantial ozone production is predicted the second day from both multiday smog chamber experiments and modeling studies. Subsequently, both NO_x and PAN concentrations decrease to very low levels unless fresh emissions are available. Although the background NO_x concentrations may be sufficient to continue low rates of ozone production during subsequent days, dilution and deposition over land result in substantial reductions in ozone concentrations. Over water, the depletion of ozone is slower owing to negligible deposition of ozone. A positive correlation was obtained in the statistical studies mentioned above between ozone and previous day NO_x emissions. Therefore, a number of types of studies indicate that NO_x should be the limiting species on the second and subsequent days.

In modeling studies of ozone production in the "clean" troposphere, a background of about 40 ppbv of ozone is predicted at 1 km. The ozone production in "clean" troposphere is NO_x limited. The concentration of PAN can exceed that of NO_x in the free troposphere; thus, PAN as a reservoir of NO_x is important in the "clean" atmosphere as well as in the aged urban plume.

Conclusions

1. Concentrations of ozone exceeding 120 ppbv are observed at nonurban locations in the northeastern, midwestern, and southeastern United States but not at locations remote from urban areas in the western United States.

2. The highest ozone concentrations observed at nonurban locations have often been reported when fumigation of the site by an urban plume occurs during passage of a high pressure system through the same region of the country.

3. Concentrations of ozone exceeding 120 ppbv have been reported at coastal locations when back trajectory analyses indicate transport starting from a populated area with subsequent passage for 24 to 48 hours over the ocean. Slow depletion of ozone is reasonable in such circumstances because of the negligible deposition of ozone over water.

4. The best direct evidence for multiday transport of ozone involves transport for 24 to 48 hour periods over the ocean. Evidence for substantial survival of ozone into the second day of transport is available over land, but multiday transport of ozone over land is largely based on circumstantial evidence.

5. Mean O_3 concentrations do not show large variations among nonurban locations across the United States, and especially small variations are reported among locations in the same region.

6. Although natural processes for O_3 formation appear likely candidates to account for mean O_3 concentrations especially in more lightly populated agricultural or forecasted areas, the available assessments do not confirm natural processes as the major sources for the O_3.

7. Photochemical O_3 formation in the free troposphere from precursors which, to a substantial extent, are of anthropogenic origin appears to account for a major part of the mean O_3 concentrations measured in nonurban areas during the warmer months of the year. Ozone formation by this process is sensitive to the vertical NO_x distributions and the contribution from anthropogenic NO_x emissions.

8. Field experiments, model studies, statistical and smog chamber experiments do not indicate that ozone formation is NO_x limited during the first day of transport downwind from urban areas.

9. For multiday transport without added emissions of precursors, NO_x does appear to be the limiting precursor. Experimental and modeling results indicate that NO_x is largely depleted before the second day of transport. The PANs and NO_x reservoir should be largely depleted also during the second day of transport in the absence of fresh NO_x emissions.

Recommendations

1. The treatment of some of the experimental results in the SURE data base (Martinez and Singh, 1979) should be extended to include the entire data base as well as other data bases available in St. Louis and the Ohio valley.

2. Multiday transport modeling studies involving air parcel movements over land and ocean areas have been conducted in Europe. Similar simplified modeling approaches can be applied now and can be used over large areas of the United States and adjacent ocean areas where there are no plans to employ Eulerian regional scale ozone models.

3. A number of modeling studies consistently indicate a significant background of ozone throughout the troposphere as a result of *in situ* ozone formation in the free troposphere. Anthropogenic emissions of NO_x, CO, and NMHC appear to make substantial contributions to ozone formation. However, none of the models have been exercised using a range of scenarios with respect to anthropogenic and biogenic emissions at midlatitudes in the northern hemisphere. Such modeling scenarios would better evaluate the portion of the ozone background potentially controllable by reductions in anthropogenic NO_x emissions.

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